

LOW ACID PRODUCING SOLID PROPELLANTS

Dr. Robert R. Bennett
Thiokol Corp., Mail Stop 243
P.O. Box 707
Brigham City, Utah 84302

Abstract

The potential environmental effects of the exhaust products of conventional rocket propellants have been assessed by various groups. Areas of concern have included stratospheric ozone, acid rain, toxicity, air quality and global warming. Some of the studies which have been performed on this subject have concluded that while the impacts of rocket use are extremely small, there are propellant development options which have the potential to reduce those impacts even further. This paper discusses the various solid propellant options which have been proposed as being more environmentally benign than current systems by reducing HCl emissions. These options include acid neutralized, acid scavenged, and nonchlorine propellants. An assessment of the acid reducing potential and the viability of each of these options is made, based on current information. Such an assessment is needed in order to judge whether the potential improvements justify the expenditures of developing the new propellant systems.

Introduction

A good deal of effort has been expended in recent years to develop and demonstrate solid rocket propellants which are more environmentally benign. These alternate propellants have often been grouped together and termed 'clean' propellants, but this appellation is misleading and tends to cloud the issue since each of the various propellant options has its own merits and drawbacks. From what is currently known, there are no rocket propellants, liquid oxygen/liquid hydrogen systems included, which are completely benign to the environment. This paper is an assessment of the various low acid solid propellant options either available or at some stage of development, with particular focus on recent solid propellant work. Although most of the published literature (NASA, Prather, Schmalzer (1985, 1986), Potter, Bennett (1992), AIAA), focuses on the environmental impact of burning propellants, it must be kept in mind that the testing and launching of rockets represents only a part of their impact. In order to make a complete assessment of the various propellant systems, one must look at the entire 'cradle to grave' impact. This includes not only the end use of the rockets, but also their manufacture, the manufacture of all the components, the disposal of waste generated in the manufacturing process, and the disposal of unwanted components in the future.

A report issued by the AIAA in October 1991 (AIAA) concluded that the use of rockets with the current production propellants has a very minor impact on the environment. However, in spite of the technical evidence of a very minor environmental impact, if substances emitted during the manufacture or use of rockets are regulated, restricted, or banned, alternate processes or fuel formulations may be required. The example is given (Hawkins) of HCl as an emission product which technically appears to have very little environmental impact, but which has been attacked in the press as a harmful to the environment (Halverson), and which may be subjected to stringent emission regulations in the future.

In order to make a rational decision about which rocket fuel to use for a propulsion system, a detailed cost/benefit analysis must be performed. Changing from a conventional fuel to one of the alternates on the basis of environmental impact does not mean simply pouring the new propellant into a rocket chamber in place of the old fuel. One must also consider the impact to the system performance,

hazards, reliability, cost, operability, material availability, and long term system stability, and decide whether or not the expected improved environmental impact is worth the price.

Discussion

Many more factors besides the specific target environmental issue must be addressed prior to the serious consideration of a propellant for use in a rocket motor. In order for a rocket motor to meet its mission requirements, it must have sufficient thrust to deliver its payload. The performance of a propellant in a given system will be a function of its specific impulse, the mass of propellant used, and the overall system weight. These, in turn, are dependent upon such things as the chemical makeup of the propellant, the propellant density, the motor chamber pressure and temperature, the reproducibility and magnitude of the propellant mechanical and ballistic properties, and the erosion characteristics of the nozzle and insulation materials.

Cost will always be a system driver, especially in commercial launch vehicles. Cost of the raw materials themselves is only a part of the system costs to which the propellant contributes. Manufacturing of motors must be considered. If the process is very labor or time intensive, cost is added, as it is if special environmental conditions for storage of materials or motors are required. The fulfilling all of the environmental regulation requirements, including waste disposal, is becoming increasingly expensive, and may be a major cost driver.

Material hazards before, during, and after mixing, will always be a concern. The propellant hazards classification, 1.1 (detonable at more than a 69 card gap) or 1.3 (non-detonable at more than a 69 card gap), usually impacts propellant formulation development. For example it is questionable whether a class 1.1 propellant (or perhaps even a class 1.1 ingredient in a class 1.3 propellant) would ever be approved for manned flight use in the U.S. Individual material hazards, such as aluminum dusting or isocyanate (propellant curative) toxicity, must be controlled during propellant process.

System reliability has always been a major concern in the rocket industry, and is especially important for manned space flight and very expensive satellite launches. System reliability depends in many ways upon the propellant used, including the reproducibility of propellant ballistic and mechanical properties, the consistency in the propellant ignition, satisfactory safety factors, and the complexity and soundness of the propellant grain design. The operability of a system is important in maintaining mission flexibility and minimizing costs. Questions such as how quickly a motor can be put onto the launch pad and readied for launch, how many environmental restrictions are required, how long the motor may be left on the pad, and how much turnaround time is required after the launch must all be addressed before a propellant system can be used.

Finally, the availability of materials must be considered. A propellant may have all of the properties one desires, but if one or more of its component materials is not readily available in sufficient quantities, it cannot be considered for production. Factors such as the scale of raw material production, the manufacturing location and frequency are important considerations.

The development of 'clean' propellants has been an evolutionary process. The issues of launch site acidification and stratospheric ozone impact were identified and addressed in the Space Shuttle Environmental Impact Statement (NASA). Although the authors were working with limited data, they concluded that both impacts would be minor and the Shuttle program proceeded. The amount of data available on both issues has increased significantly in recent years, but the original conclusions of a minor impact remain the same. However, public awareness of these and other environmental issues has been greatly heightened, as has the number of environmental regulations. As a result, in the 1980s, a number of 'clean' propellant programs were begun to specifically address the acidification

issue. This paper will deal only with the HCl issue. Additional reviews have been published by the author regarding the impacts of chemical propulsion on the stratospheric ozone (e.g. Bennett (1992)).

Acid Production and Propellant Options

The deposition of acidic species on the area around the Space Shuttle launch pads at the Kennedy Space Center and their impact on the local environment is well documented (Schmalzer (1985, 1986)). On a regional or global scale, acid deposition due to the HCl in solid rocket exhaust represents an extremely small portion of acidic species deposited in the atmosphere. If only anthropogenic sources in the U.S. are considered, heating and power production deposit about 33,000 kilotons of acid producing chemicals (mainly sulfur oxides and nitrogen oxides) into the atmosphere annually; transportation about 9,100 kilotons; and industrial processes about 6,100 kilotons (Schwartz). This compares with about 2.3 kilotons (of HCl) from chemical propulsion systems worldwide (1.8 kilotons from U. S. launches) at the 1991 launch rate estimated in the AIAA workshop report. The global impact will be smaller still. HCl is a very common tropospheric species, produced naturally by the reaction of sodium chloride in marine aerosols with atmospheric nitric acid. One estimate is that worldwide, the oceans alone produce about 330,000 kilotons of HCl annually (Symonds).

On a local level, Space Shuttle launches at Kennedy Space Center cause near field (< 2,500 ft) acidification effects due to the SRB (Solid Rocket Booster) exhaust (Schmalzer (1985, 1986)). There are some fish and plant mortalities and a reduction in plant speciation, but only in a very localized area of about 0.08 square miles near each of the two launch pads. Far field acid effects (> 2,500 ft) seem to be limited to leaf spotting as the exhaust plume is dispersed over a wide area.

In order to put the extent of the near field area affected by the HCl into perspective, a comparison was made of the area at the Kennedy Space Center permanently affected by near-field acidification with that affected by buildings, roads, parking lots, launch pads and landing facilities. The KSC buildings occupy 0.13 sq. miles, which is almost as much area as is affected by the HCl cloud. When the roads, parking lots, launch pads and landing facilities are included, an area of 1.6 sq. miles has been covered. This means the HCl from the SRB exhaust permanently affects the flora and fauna of an area which is about 10 percent as large as the area completely covered by other facilities.

In spite of what seems to be a relatively minor impact, the development of reduced acid propellants continues for several reasons. The technical evidence notwithstanding, the perception reflected in the popular press has been that the problem is significant. At least two lawsuits were filed to prevent NASA from proceeding with the testing of the Advanced Solid Rocket Motor (ASRM) in Mississippi on environmental grounds (Space News). Political decisions are often made on the basis of public opinion rather than technical facts. Since HCl emissions may very well be regulated in the future, it is important to have a back-up system from which HCl emissions have been substantially reduced. Finally, though it appears unlikely at this time, there may be long-term environmental effects of HCl which have not yet been detected, and which would make the use of low HCl propellants desirable.

Several options exist for reducing the amount of HCl in the propellant exhaust. They can be subdivided into various families: neutralized, scavenged, and nonchlorine; each of which has its own unique challenges and advantages which are a function of the chemistry and physical properties of the materials used. Table I lists the major categories of solid propellants to be discussed, their primary constituents and exhaust products, and their density and specific impulse. For the products listed in Table I, it was assumed that all of the hydrogen and carbon monoxide emitted react with atmospheric oxygen to form water and carbon dioxide. This is likely true for altitudes below about 25 km. Model calculations also suggest that some of the HCl produced in the motor chamber is converted to Cl_2 in the

TABLE I
The Composition and Exhaust Products of Conventional and Alternate Solid Propellants

Propellant Ingredient	Purpose	Space Shuttle	Nominal Class 1.1	Neut.	Scav.	HAN/AN	Nitrate Ester Plast. AN	GAP/AN	PGN/AN
PBAN/ECA	Binder	14.00							
HTPB/NCO	Binder			12.00	10.00				
PEG/NCO	Binder		7.00						
PGA/NCO	Binder						5.91		
GAP/NCO	Binder							20.90	
PGN/NCO	Binder								20.90
PVA	Binder					15.00			
NG	Plasticizer		17.00						
BuNENA	Plasticizer						16.09		
AP	Oxidizer	69.75	8.00	65.70	29.54				
AN	Oxidizer					3.25	51.00	52.00	52.00
HMX	Oxidizer		47.00		15.00				
NaNO ₃	Oxidizer				23.21				
HAN	Oxidizer					57.20			
KClO ₄	Oxidizer							5.00	5.00
Aluminum	Fuel	16.00	20.00		22.00	20.00	13.50	21.00	21.00
Magnesium	Fuel			22.00			13.50		
MNA	Stabilizer		0.50						
2-NDPA	Stabilizer		0.20						
NC	Crosslinker		0.30						
Fe ₂ O ₃	Ball. Accel.	0.25		0.30	0.25			0.60	0.60
Carbon	Additive							0.50	0.50
H ₂ O	Additive					0.33			
Amphos	Additive					0.65			
BIPY	Additive					0.65			
GNX	Additive					2.60			
Dequest	Additive					0.32			
Isp(vac)		285.3	295.6	281.1	273.3	279.9	283.9	277.9	278.1
Density		0.06408	0.06707	0.06075	0.06898	0.06321	0.05910	0.06398	0.06578
Isp*Density ^{0.6}	54.87	58.43	52.35	54.94	53.39	52.01	53.40	54.33	
Major Exhaust Products		Mass Produced/100g Propellant Burned^a							
HCl		19.22	2.11	0-14.5 ^c	1.44	0.89		0.18	0.39
Cl ₂ ^d		2.14	0.23	<1.4	0.16	0.10		0.02	0.04
H ₂ O		28.35	21.95	28.34	22.03	37.80	36.88	33.66	31.82
CO ₂		41.67	55.18	37.55	40.04	33.44	34.20	30.73	26.66
Al ₂ O ₃		30.43	36.48		41.69	37.96		39.89	39.98
NOx ^b		6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
N ₂		8.78	21.42	6.72	13.21	19.24	21.12	26.76	20.89
Mg(OH) ₂				30-45 ^c			17.73		
MgCl ₂				5-22 ^e					
NaCl					12.08				
Na[O] ^f					>1.50				
KCl								2.28	1.82
K[O] ^f								>0.18	>0.33
MgAl ₂ O ₄							35.60		

TABLE I (cont.)
The Composition and Exhaust Products of Conventional and Alternate Solid Propellants

Propellant Ingredient	Purpose	TEP ^d	Minimum Smoke
Nitrocellulose	Binder	yes	
PEG/NCO	Binder		3.00
PCP/NCO	Binder		2.91
BTTN	Plasticizer	yes	15.23
TMETN	Plasticizer		7.61
AN	Oxidizer	yes	
HMX	Oxidizer		20.25
RDX	Oxidizer		47.25
Aluminum	Fuel	yes	
MNA	Stabilizer	yes	0.50
Various Additives			3.25
Isp(vac)		285	268.6
Density		0.066	0.06187
Isp*Density ^{a, e}		55.80	50.58

Major Exhaust Products	Mass Produced/100g Propellant Burned ^a
HCl	
Cl ₂ ^d	
H ₂ O	28.01
CO ₂	73.81
Al ₂ O ₃	1.00
NO _x ^b	6.0
N ₂	29.65
Ph	1.35

^aAssumes all H₂ is converted to H₂O, and all CO to CO₂.

^bNO_x estimate for Shuttle based on data in (Karol). Other propellants assumed to produce the same relative amount.

^cActual values depend on effectiveness of neutralization process. Lab data suggests HCl produced is at least less than 3%. MgO is an nozzle exit species of this propellant. The table assumes that all MgO is hydrated and converted to Mg(OH)₂. Thermochemical calculations predict 4.8 g MgCl₂/100 g propellant at the nozzle exit plane. 22 g will be produced if all HCl is neutralized.

^dThermochemical code predicts essentially no Cl₂ at the nozzle exit, but some is produced during afterburning. Measurements of captured exhaust plumes of Shuttle propellant at Thiokol show that about 10% of the HCl is converted to Cl₂. The same HCl/Cl₂ ratio is assumed for other propellants.

^eThermochemical code predicts elemental sodium or potassium at the nozzle exit plane. They will certainly be oxidized in the plume, but the final compounds produced are not known.

^fFormulation is proprietary, however, propellant contains no chlorine.

plume. Various estimates of the extent of this reaction have been given (NASA, Hoshizaki). The values given in Table I assume that the models for HCl vs. Cl_2 cited in (NASA) are correct since they are consistent with experimental measurements made at Thiokol Corp. The NO_x production from afterburning is based on data given by Karol et al. (Karol), and is fairly consistent with NO_x measurements obtained from an airborne flythrough of a Titan launch (Stewart).

Neutralized Propellants

The first of the three families of reduced acid propellants relies on simple acid-base chemistry to neutralize the HCl in the exhaust plume (Doll). In the neutralized propellants, magnesium is used in the place of aluminum as the metal fuel. All other ingredients remain essentially the same. Approximately 70 percent of the formulation by weight is ammonium perchlorate, 12-14 percent is polymeric binder, and 16-18 percent is magnesium. As the propellant burns, the magnesium is oxidized to form magnesium oxide (eq. (1)). Upon contact with water, the magnesium oxide forms magnesium hydroxide (eq. (2)). This is a very basic material, which reacts readily with HCl to form magnesium chloride and water (eq. (3)).



It was shown in the laboratory and in small scale motors that the neutralization reaction does indeed occur, and also that water is an essential component of the mechanism. The lab data suggested that the neutralization reaction has the potential of completely removing HCl from the exhaust plume, almost certainly if a $\text{MgO}/\text{H}_2\text{O}/\text{HCl}$ aerosol is formed. In order to better assess the extent of neutralization in a more realistic environment, a 2000 lb motor containing this propellant was static tested, with an array of HCl measuring devices, including an airborne instrument platform (Bennett (1993)). It was found in this test that only about 1/2 of the HCl was neutralized, apparently because of the rapid dispersion of the exhaust cloud. For aerosol deposition such as that observed with the Shuttle launches as the plume mixes with the sound suppression water, the data still suggest that complete neutralization would occur.

As outlined above, there are several other factors which must be evaluated prior to seriously considering the use of a propellant in a rocket motor. For the neutralized propellant, the processing is essentially the same as conventional propellants, so the waste generation and disposal would remain unchanged. The specific impulse of the neutralized propellant is close to that of conventional aluminized propellants (281.8 vs. 285.3), but the density is considerably lower (0.0591 vs. 0.0641 lb/in^3). It is unlikely that this would be an acceptable option for a retrofit of an existing volume limited motor, but it would be a potential candidate for a new system designed specifically for its properties. Table I compares the theoretical performance for a typical first stage or booster application for the nominal Class 1.3 Space Shuttle propellant along with the various alternate formulations. For this application, it is estimated that the performance is equal to the product of the specific impulse and the density raised to the 0.6 power. Among the ten propellants evaluated, the neutralized propellant ranks eighth in total performance in a volume limited system because of its low density.

The cost of such a system would be about the same as conventional motors, since all materials but one are the same. The only additional processing concern would be that the magnesium needs to stay as dry as possible. An extensive hazards characterization has been performed on this propellant under the Solid Propulsion Integration and Verification (SPIV) program (Cragun), and has shown it to be Class 1.3 similar to the Space Shuttle and Peacekeeper Stage I propellants. A full scale propellant and bondline characterization study has been performed, and shows the neutralized propellant to be

robust and versatile. Propellant aging capability is still largely unknown. From the available data, reliability, operability and material availability should be comparable to existing systems. Of the proposed alternate solid propellants, the neutralized and scavenged propellants are the most mature.

Scavenged Propellants

The second of the reduced acid propellant families are the scavenged propellants. In these propellants, sodium nitrate is used in place of about 1/2 of the AP. As the propellant burns in the rocket chamber, the sodium ions scavenge most of the chloride ions to form NaCl, preventing them from forming HCl. Laboratory measurements and theoretical calculations indicate that the HCl emissions are reduced by about an order of magnitude from conventional propellants. An accurate quantification of the acid reducing capability of the scavenged propellants during an open air test has not yet been made, although there are plans to do so in the future.

Replacement of AP with sodium nitrate exacts a specific impulse penalty. Depending on the formulation, 15 - 20 seconds are lost compared to conventional Space Shuttle propellant. Some of this (5 - 10 seconds) is regained if an energetic nitramine, such as HMX, is used (Table I), but attaining Space Shuttle Isp with a sodium nitrate propellant is not realistic. However, because of its increased density of sodium nitrate over AP, a scavenged propellant appears to be practical in a volume limited, booster/first stage application. The loss in specific impulse can be compensated for by virtue of the fact that a greater mass of propellant can be used in the motor. It appears that essentially the same overall performance as the Space Shuttle can be achieved in a scavenged propellant by a combination of the addition of HMX and a higher solids loading. Table I shows that a scavenged propellant formulated at 90 percent solids and 15 percent HMX has total performance ($I_{sp} \times \text{density}^{0.6}$) of 54.94 compared with Space Shuttle's 54.87.

As with the magnesium propellant, conventional processing techniques would be used for the scavenged propellant, with about the same amount of waste generation. Material costs would be slightly higher if HMX were used. Manufacturing costs might also be somewhat higher because a larger number of ingredients means more storage space and material control work. Though a complete hazards characterization has not yet been performed, the tests run to date show the hazards of the scavenged propellants to be about the same as those of conventional class 1.3 composite propellants. HMX is a Class 1.1 material, but it can be used in moderate amounts without making the propellant Class 1.1. In fact at least 15 percent HMX can be added without detonating a zero card gap pipe.

Sodium nitrate formulations have been scaled up to full scale (600 gallon) mixes, and have been tested in motors of various sizes up to about 2000 lb, showing the expected properties. Mechanical properties are not as robust as the neutralized propellants, with somewhat lower strain capability, but they appear to be about as good as the conventional Minuteman Stage I propellant (30 percent strain and 130 psi maximum corrected stress). The reliability of the propellant should be reasonably good, though the increased number of ingredients may result in somewhat higher propellant variability, but this is purely speculative. Operability and availability of materials are likely to be about the same as for conventional propellants.

Reduced Chlorine Propellants

The final family of reduced acid propellants does not depend on the acid neutralization or scavenging reactions to reduce the acid in the exhaust, it simply contains little or no chlorine in the first place. A wide variety of approaches exist for reducing the amount of chlorine in the propellants, and each presents its own set of challenges or drawbacks. In concept, the simplest approach is to replace

the AP with a nonchlorine oxidizer.

For class 1.3 composite propellants, ammonium nitrate (AN) has been extensively studied. More recently, the more energetic hydroxyl ammonium nitrate (HAN) has been used in conjunction with AN to form a eutectic mixture which is a liquid at room temperature. This liquid oxidizer has then been mixed with polyvinyl alcohol and aluminum (if desired) to form a gel propellant (Katzakian). Other potential oxidizers such as ammonium dinitramide (ADN) are under preliminary investigation on the lab scale. Since the replacement of AP by AN results in a substantial performance loss and very limited ballistic tailorability, more energetic binder and plasticizer systems are being investigated.

AN presents other challenges in addition to lower performance capability. Studies to date have shown little ballistic or mechanical property tailorability. AN propellant burn rate is typically quite low, and burn rate slope quite high. The mechanical property capability of AN propellants has generally been rather poor, with strains in the 10 - 20 percent range at a stress level of 160 psi (Weyland), or about 30 percent at a stress level of 80 psi (Bradford). At equivalent solids loading, processing is generally more difficult than AP propellants, and AN has a number of crystalline phase transitions in the temperature range normally associated with propellant cure and storage requirements. Since the different phases have different densities, if the AN crystalline phase is not stabilized by an additive, the propellant grain tends to increase in volume as it is temperature cycled, disrupting its integrity. AN is also more moisture sensitive than AP. While none of these difficulties appears insurmountable, they do represent a significant challenge to propellant chemists and engineers. AN propellants have been static tested in at least 70 lb. motors.

As mentioned, energetic polymers and plasticizers have been considered for some time in connection with improving the performance of AN oxidized propellants. Among those polymers considered are glycidyl azide polymer (GAP), polyglycidyl nitrate (PGN), polyoxetanes, and polynitramines. Some of these materials are available in large enough quantities to be considered for production propellants.

One promising new approach under investigation by Thiokol, given the acronym TEP, is to use a nitrate ester to plasticize and gel nitrocellulose. Although this ingredient combination has been used for quite some time, unique processing techniques have imparted greatly improved mechanical properties, with strains of about 100 percent and stresses approaching 1000 psi. Aluminum and ammonium nitrate can be added to improve performance, with performance identical to Space Shuttle easily achievable. Minimum signature TEP formulations have been shown to be Class 1.3. The processing and gel mechanisms of TEP and other gelled solid propellants are considerably different than conventional propellants. No chemical cross linking is employed, giving them the potential to significantly reduced propellant waste streams. In addition, the TEP propellant has an indefinite working life and is insensitive to low levels of moisture contamination. Nitrate ester plasticizers have been used in other AN propellant formulations as well. These propellants show some promise, but are not mature enough to know if they are viable for production motors.

The HAN/AN gel propellants exhibit greatly improved strain capability (in excess of 250 percent) over conventional class 1.3 composite propellants (Katzakian). A HAN/AN propellant has been tested in an 800 lb Super BATES motor at Edwards AFB. The HAN/AN/PVA binder system is water soluble, so motors could conceivably be washed out easily; however, this very fact raises concerns about aging this propellant with exposure to atmospheric humidity. Both the specific impulse and the density of the HAN/AN propellants are lower than conventional Shuttle propellant, so motors could not likely be retrofit with them. While some success has been achieved in tailoring the HAN/AN propellant burn rate, the burn rate exponent remains higher than is desirable (> 0.6).

Cost, reliability, operability, hazards, aging characteristics, and material availability all remain

open issues with the Class 1.3 AN and gel systems. They are considerably less mature than the scavenged and neutralized propellants. While ADN looks promising on paper, it is currently available in very limited quantities in the U.S., although the Soviet Union apparently produced a large amount of the material for some time (Pak). It still appears that the practical use of ADN in U.S. rocket motors is at least several years distant.

If the Class 1.3 requirement does not apply, conventional high energy, Class 1.1 propellants can be used in order to reduce the HCl in the exhaust. These generally consist of polyethylene or polyester binders, plasticized with nitrate esters. HMX is used as the main solid oxidizer, with only 8-10 percent AP present for ballistic tailoring. These propellants have been used for years in submarine launched ballistic missiles such as C-4 and D-5, and in tactical minimum smoke applications. When aluminized, they outperform the conventional class 1.3 composite propellants (Table I), are easily processed and have excellent mechanical and ballistic property capabilities, both as produced and with aging. They typically cost more than Class 1.3 propellants, because of the price of the nitrate esters and the HMX. Reliability and availability of materials are similar to Class 1.3 propellants. Their major perceived drawback is their hazards properties, since by definition they will detonate at greater than 69 cards, and hence have very small critical diameters. This could impact operability for space launch systems. Despite the potential for detonation, motors loaded with Class 1.1 propellants enjoy a very good safety record in the field; however, none of the current space launch vehicles use this family of propellants.

In summary, there are several approaches to reducing the acid content of the exhaust plume. The most mature are the conventional high energy Class 1.1 propellants, which have been in production for many years, but are viewed as being more hazardous than the Class 1.3 propellants. For the Class 1.3 propellants, the neutralized and scavenged propellants are the most mature, having been made in full scale mixes, cast and tested in large subscale motors, and characterized extensively. The AN propellants, both gel and conventional, are not as mature, and have more technical challenges to be overcome. The extent of acid reduction by the magnesium neutralized propellants depends on the environmental conditions under which it is used, and is in the range of 0 - 10 percent. The sodium nitrate and high energy propellants have the potential of reducing the HCl in the exhaust by about an order of magnitude, to 1-3 percent, while the nonchlorine propellants eliminate it entirely.

References

1. AIAA, 'Atmospheric Effects of Chemical Rocket Propulsion,' October 1991, Report of an AIAA Workshop held in Sacramento, California, 28-29 June, 1991.
2. Bennett, R. R., Wallace, I. A., Richtsmeier, S. C., and Goldstein, N., 'Characterization of the Exhaust Cloud of a 37-Inch Magnesium Fueled Rocket Motor,' 1993 JANNAF Safety and Environmental Protection Subcommittee Meeting, Las Cruces, NM, August 10, 1993.
3. Bennett, R. R., Hinshaw, J. C., and Barnes, M. W., 'The Effects of Chemical Propulsion on the Environment,' *Acta. Astronautica* 26(7), 531 (1992).
4. Bradford, D. J., et al., 'Clean Propellant Development Demonstration,' report prepared for the Astronautics Laboratory (AFSC), Contract No. FO4611-89-C-0082, Report Nos. 13 and 16, 1991.
5. Cragun, B. C., 'Hazards Properties of a Magnesium Neutralized Clean Propellant,' paper presented at the 1992 JANNAF Prop. Sys. Haz. Sub. Conference, Silver Springs MD, April 1992.
6. Doll, D. W. and Lund, G. K., 'Magnesium-neutralized Clean Propellant,' paper No. AIAA-91-

- 2560, presented at the 27th AIAA Joint Propulsion Conference, Sacramento, CA June 24-26, 1991.
7. Halverson, T., 'Proposed Rocket Tests Puts NASA on the Defensive,' *Flor. Today*, Oct. 28, 1991.
8. Hawkins, T. W. and Wilkerson, B. E., 'Environmental Propellant: Current Issues and Assessment,' 1992 JANNAF Propulsion Meeting, Indianapolis, Indiana.
9. Hoshizaki, H. et al, 'Aircraft Wake Microscale Phenomena,' in *The Stratosphere Perturbed by Propulsion Effluents*, Climate Impact Assessment Program, Monograph 3, DOT-TST-75-53, U. S. Department of Transportation, September 1975, p. 2-68.
10. Karol, I. L., Ozolin, Y. E., and Rozanov, E. V., 'Effect of Space Rocket Launches on Ozone and Other Atmospheric Gases,' presented at a European Geophysical Assoc. Conference, Wiesbaden, 1991.
11. Katzakian, A., Jr., 'Alternate Clean Propellant Development,' report prepared for the Astronautics Laboratory (AFSC), Report No. LHL-M-04, 20 October 1990; Katzakian, A., Jr., Bruenner, R. S., Clark, G. M., Grix, C. E., Lou, R. L., and Oberth, A., E., 'Development of a New High Performance Clean Solid Propellant,' paper presented at the 1992 JANNAF Propellant Development and Characterization Subcommittee Meeting, Kennedy Space Center, Florida, 7-9 April, 1992.
12. NASA, 'Space Shuttle Program Environmental Impact Statement,' April, 1978.
13. Pak, Z. 'Some Ways to Higher Environmental Safety of Solid Rocket Propellant Application,' Paper #AIAA-93-1755, AIAA 29th Joint Propulsion Conference, Monterey, CA, June 28-30, 1993
14. Potter, A. E., 'Environmental Effects of the Space Shuttle,' *J. Environ. Sci.*, 21, 15 (1978).
15. Prather, M., Garcia, M. M., Douglass, A. R., Jackman, C. H., Ko, M. K. W., and Sze, N. D., 'The Space Shuttle's Impact on the Stratosphere,' *J. Geophys. Res.* 95(D11), 18,583 (1990).
16. Schmalzer, P. A., Hinkle, C. R., and Breining, D., 'Effects of Space Shuttle Launches STS-1 Through STS-9 on Terrestrial Vegetation of John F. Kennedy Space Center, Florida,' NASA Tech.
17. Schmalzer, P. A., Hinkle, C. R., and Dreschel, T. W., 'Far-Field Deposition from Space Shuttle Launches at John F. Kennedy Space Center, Florida,' NASA Tech. Mem. 83104 (1986).
18. Schwartz, S. E., 'Acid Deposition: Unravelling a Regional Phenomenon,' *Science* 243, 753 (1989); Robinson, E. and Robbins, R. C., 'Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants,' Stanford Research Institute, Report SRI Project PR-6755, February 1968. Supplemental Report, June, 1969; National Acid Precipitation Assessment Program, 'Interim Assessment: The Causes and Effects of Acidic Deposition,' (Government Printing Office, Washington, D. C. 1987).
19. Space News, 'Lawsuits Threaten ASRM Tests,' November 4-10, 1991.
20. Stewart, R. B. and Gomberg, R. I., 'The Production of Nitric Oxide in the Troposphere as a Result of Solid-Rocket-Motor Afterburning,' NASA Technical Note D-8137, March 1976.
21. Symonds, R., Rose, W., and Reed, M., 'Contribution of Cl and F Bearing Gases to the Atmosphere by Volcanoes,' *Nature* 334, 415 (1989).
22. Weyland, H. H. and Miller, R. R., 'Clean Propellant for Large Solid Rocket Motors,' Final report prepared for the Astronautics Laboratory (AFSC), Report No. AL-TR-90-016, 1990.